

## POTENTIAL DISTRIBUTION IN A TRICKLE-BED ELECTRODE

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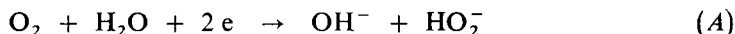
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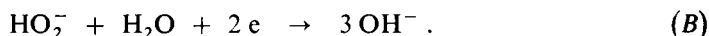
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The performance of trickle-bed electrodes of crushed graphites in oxygen reduction to hydrogen peroxide has been investigated. Results are presented for the effects of the current density, gas and electrolyte flow rates, pressure, and graphite particle size on the electrode potential, voltage loss in the electrode material, and current yield of the process.

The reduction of oxygen on carbonaceous materials in alkaline media gives rise to perhydroxyl ions:



Only at more negative potentials (for graphite, more negative than 0.5 V with respect to the equilibrium potential of hydrogen electrode in the same solution<sup>1</sup>) do the perhydroxyl ions start undergoing reduction according to the equation



The reduction of oxygen to hydrogen peroxide in alkaline medium is of practical interest because of its potential for the production of hydrogen peroxide with low consumption of electrical energy.

Over the last decade, the interest has been focused primarily on the study of this process in trickle-bed electrodes<sup>2-9</sup>, since these are easier to make and are less mechanically sensitive than gas diffusion electrodes. The above cited studies deal with the effects of various parameters (current density, gas and electrolyte flow rates, pressure) on the current yields of hydrogen peroxide and the total voltage on the electrolyzer. The potential of trickle-bed electrodes has only been measured to a limited extent<sup>4,5,7</sup>.

Since the electrode potential has a substantial effect on the current yield of hydrogen peroxide, we have investigated its values in various parts of a trickle-bed electrode under various conditions of electrolysis.

## EXPERIMENTAL

A cross-section of the electrolytic cell used in the study of the trickle-bed electrode is shown in Fig. 1. The electrode material is compressed between stainless steel plate 1, which serves as the current collector, and diaphragm or ion-exchange membrane 3. The anode consists of a nickel-plated stainless steel plate 2. The electrolyte (2M-NaOH) and oxygen are fed into injector 4, pass through the trickle-bed electrode, and leave the cell through tube 6. In the diaphragm arrangement, the anode compartment is closed and the electrolyte ions get to the anode solely by transport through the diaphragm. When a membrane is used, the anolyte enters the cell through tube 7, and leaves it through tube 8.

Three potential probes 9 extend into the trickle-bed electrode at distances of 50, 250, and 450 mm from the point of gas and electrolyte entry. Each probe is held by a screw joint 10 with seal 11. This makes the cell leak tight up to a pressure of 1 MPa, and permits axial movement of the probe. The potential probes consist of polyamide tubes 6 mm in diameter, sealed at the ends facing the diaphragm. Four 0.7 mm diameter openings around the perimeter of each probe face make it possible to measure the potential of the adjacent particles of the electrode material. All measured potentials are reported relative to a reference mercuric oxide electrode in 2M-NaOH.

The measured voltage between the reference electrode and the current collector was used directly to evaluate the potential,  $E'$ , which includes the local potential,  $E$ , and the ohmic loss,

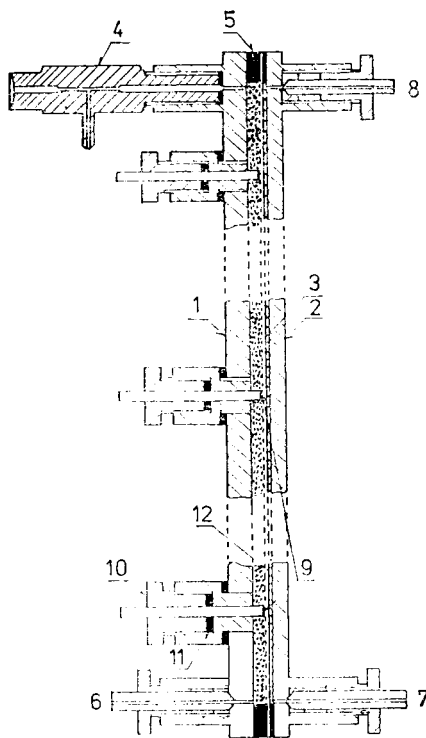


FIG. 1

A cross-section of the cell with a trickle-bed electrode. 1 cathodic current collector; 2 anode; 3 diaphragm or ionex membrane; 4 injector; 5 gasket; 6 catholyte outlet; 7 anolyte inlet; 8 anolyte outlet; 9 potential probe; 10 screw joint; 11 seal; 12 nickel mesh

$\Delta\varphi(x)$ , in the electrode material between the current collector and the measured place.

$$E'(x) = E(x) + \Delta\varphi(x) \quad (1)$$

The voltage loss,  $\Delta\varphi(t)$ , across the electrode layer during the passage of current was measured with the aid of nickel mesh 12 sandwiched between the electrode material and the diaphragm or membrane.

The resistance of the electrode materials employed was also measured in dry condition in a special vessel with the material placed inside a cylindrical cavity of 6 mm diameter and 10 mm height. A well-defined pressure within the range 10–340 kPa was applied, and the height of the layer was measured by an indicator.

The trickle-bed electrodes were 0.5 m high, 21 mm wide, and 3.3 mm thick. Four sieve fractions of S 42 graphitized carbon (product of Elektrokarbon Topoľčany, Czechoslovakia) with grain sizes of 0.08–0.18 mm (I), 0.18–0.4 mm (II), 0.4–0.63 mm (III), and 0.63–1 mm (IV) were used as the filling of the electrodes.

The electrolyte solution was supplied to the cell at room temperature (about 295 K), and the temperature within the cell was by 5 to 35 K higher, depending on the solution flow rate and the current. Other details of the experimental arrangement have been described in our previous paper<sup>9</sup>.

## RESULTS AND DISCUSSION

The local potential,  $E'$ , in trickle-bed electrodes of crushed graphite was measured at various distances from the current collector plane, i.e., at various distances between the ends of the potential probes and the plane of the steel cathodic current collector.

The measured dependences of the local potential,  $E'$ , on the distance from the current collector at various current densities are illustrated in Fig. 2. The values of the potential are averages of four measurements. As seen from the figure, the local potential decreases dramatically in the direction from the current collector to the diaphragm.

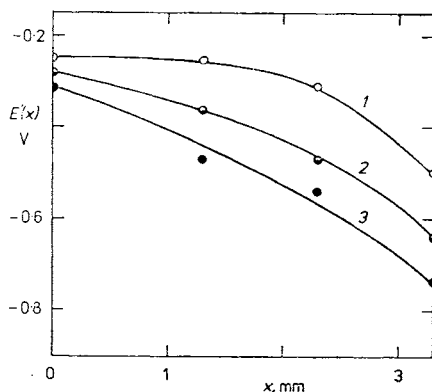


FIG. 2  
Variation in the potential,  $E'(x)$ , of S 42 graphite electrode (sieve fraction II) with the distance from the current collector plane at various current densities: 1  $0.25 \text{ kA m}^{-2}$ ; 2  $0.5 \text{ kA m}^{-2}$ ; 3  $0.75 \text{ kA m}^{-2}$ . Electrolyte flow rate,  $0.15 \text{ dm}^3 \text{ h}^{-1}$ ; oxygen flow rate,  $86 \text{ dm}^3 \text{ h}^{-1}$ ; Volpor PVC diaphragm

Characteristic values of voltage loss in the electrode material at various distances from the current collector are difficult to determine experimentally. Therefore, we have measured at least the average voltage loss,  $\Delta\phi(t)$ , across the layer of electrode material by measuring the voltage between the current collector and the nickel mesh (12 in Fig. 1). We have found that, over the potential range in which oxygen trickle-bed electrodes operate, the Faradaic currents flowing through the mesh form only 0.2 to 0.5% of the current passing through the electrode, so that the voltage loss between the mesh and the adjacent electrode material can be neglected.

The voltage loss across the electrode layer is approximately proportional to the total current flowing through the trickle-bed electrode (see Fig. 3). We have found, however, that this quantity decreases significantly on tightening the peripheral screws of the cell. This indicates that  $\Delta\phi(t)$  strongly depends on the compression of the electrode material.

Therefore, the resistance of crushed graphites has been measured as a function of the compression. The dependences of the specific resistance and the thickness of graphite layer on the compression are illustrated in Fig. 4. There is a several-fold decrease in the resistance of the material for increasing the pressure from 10 to

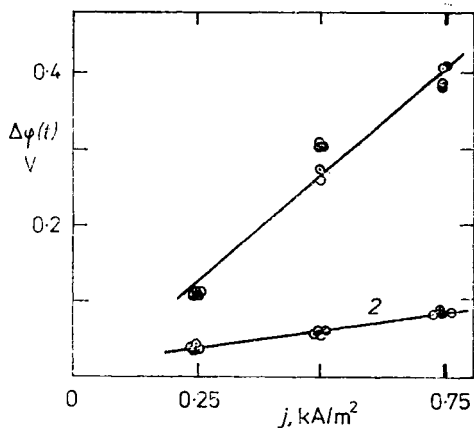


FIG. 3

A plot of the voltage loss in the solid phase of the electrode against the current density. Oxygen flow rate,  $35 \text{ dm}^3 \text{ h}^{-1}$  ( $\circ, \ominus, \bullet$ ), or  $210 \text{ dm}^3 \text{ h}^{-1}$  ( $\odot, \oplus, \bullet$ ); electrolyte flow rate,  $0.075 \text{ dm}^3 \text{ h}^{-1}$  ( $\circ, \odot$ ),  $0.15 \text{ dm}^3 \text{ h}^{-1}$  ( $\ominus, \oplus$ ), or  $0.3 \text{ dm}^3 \text{ h}^{-1}$  ( $\bullet, \bullet$ ). 1 first series of measurements; 2 measured after tightening the cell screws

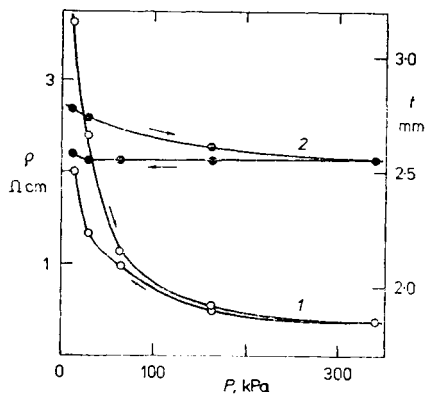


FIG. 4

Variation in 1 the specific resistance and 2 the thickness of graphite layer (fraction II) with the compression. The arrows indicate the sense in which the measurements were taken

160 kPa (see curve 1). For good performance, the trickle-bed electrode of crushed graphite requires compression of the electrode material by a pressure of at least 100 kPa. Curve 2 in the same figure shows that the compressibility of the material is very small. At 166 kPa, for example, the relative compaction of the layer is 5.8%; for a layer 3 mm thick this corresponds to 0.17 mm only. The measurements of the resistance of various sieve fractions of graphite in the range 0.08 to 1 mm have shown that the effect of the particle size on the electrical resistance of the material is insignificant relative to the scatter in experimental data.

The use of axially movable probes makes it possible to evaluate the potential at both walls of the trickle-bed electrode. The potential  $E(0)$  at the current collector was measured directly with the mouths of the probes in the plane of the current collector. The local potential of the electrode at the diaphragm,  $E(t)$ , was calculated on the basis of Eq. (1) from values of  $E'(t)$  obtained by measurements in which the probe mouths abutted on the nickel mesh at the diaphragm, and from measured values of  $\Delta\varphi(t)$ .

From the data given in Tables I and II it is seen that the potential at the diaphragm is by 0.05–0.2 V more negative than that at the current collector. This indicates that the current density is higher at the diaphragm. The increase in the local current density with the distance from the current collector is in accord with theoretical prediction for an electrode with the conductivity higher than that of the electrolyte<sup>8</sup>.

Both the wall potentials shift with increasing oxygen flow rate to more positive values (by 40 to 60 mV), in qualitative agreement with our model of trickle-bed electrode<sup>8</sup>. This is because the increase in oxygen flow rate produces an increase in the pressure loss, and hence an increase in the coefficient of oxygen transport within the electrode.

Our model of trickle-bed electrode<sup>8</sup> gives the mass transfer coefficients in the gas ( $K_G$ ) and in the liquid at the g-l ( $K_L$ ) and l-s ( $K_S$ ) interfaces as increasing with the gas and liquid flow rates, respectively. The overall mass transfer coefficient is calculated from the equation

$$K_0 = (1/K_G + 1/K_L + 1/K_S)^{-1} \quad (2)$$

derived on the simplifying assumption that the g-l and l-s interfacial areas are the same. The relationships for the local current densities of oxygen reduction, the potential profile, and the peroxide concentration in the electrode are rather complicated, and the reader is therefore referred to the original paper<sup>8</sup>.

In variance with the model, however, is the observed negative shift of the potential with increasing electrolyte flow rate (see Table II). The model assumes that the liquid-side mass transfer coefficient increases with increasing electrolyte flow rate. In real crushed graphite electrodes, however, the assumption of the equality of the g-l and l-s interfacial areas is apparently not fulfilled. We have found that the

proportion of gas in these electrodes is relatively small: even at atmospheric pressure it makes just 15 to 45% of the interparticle pore volume, and decreases markedly as the pressure is increased<sup>9</sup>. This suggests that the area of the g-l interface is smaller than that of the l-s interface. Since, according to our calculations, the oxygen transport through the liquid at the gas-liquid interface is the rate-determining step of oxygen transport within the trickle-bed electrode<sup>8</sup>, the effect of the reduction in the gas-liquid interfacial area by increasing the solution flow rate may outweigh the effect of the increase in the mass transport coefficients, resulting in a net decrease in the rate of the process.

With all the crushed graphite trickle-bed electrodes investigated, the current yield of hydrogen peroxide was observed to increase considerably with increasing solution flow rate (see, for example, Table II). Since, as mentioned above, an increase in the solution flow rate does not produce a positive shift in the potential, it follows that the positive effect of the solution flow rate on the yield is just the result of a lower peroxide concentration in the solution at an increased flow rate and of reduced

TABLE I

Average values of potentials  $E(0)$  and  $E(t)$  in a trickle-bed electrode of graphite (fraction II), and current yields of  $H_2O_2$  ( $\eta$ ) at various oxygen flow rates ( $v_G$ ). The first and parenthesized values refer to outlet overpressures of 0 and 0.2 MPa, respectively. Current density,  $0.25 \text{ kA m}^{-2}$ ; electrolyte flow rate,  $0.15 \text{ dm}^3 \text{ h}^{-1}$ ; outlet overpressures, 0 and 0.2 MPa; Volpor PVC diaphragm

$v_G, \text{ dm}^3 \text{ h}^{-1}$	$E(0), \text{ V}$	$E(t), \text{ V}$	$\eta, \%$
34	-0.283 (-0.230)	-0.398 (-0.302)	45 (57)
86	-0.256 (-0.199)	-0.393 (-0.253)	49 (63)
136	-0.235 (-0.186)	-0.363 (-0.245)	51 (64)

TABLE II

Average values of potentials  $E(0)$  and  $E(t)$  in a trickle-bed electrode of graphite (fraction II), and current yields of  $H_2O_2$  ( $\eta$ ) at various electrolyte flow rates ( $v_L$ ). Oxygen flow rate,  $86 \text{ dm}^3 \text{ h}^{-1}$ ; other conditions are the same as those of Table I

$v_L, \text{ cm}^3 \text{ h}^{-1}$	$E(0), \text{ V}$	$E(t), \text{ V}$	$\eta, \%$
300	-0.278 (-0.204)	-0.509 (-0.312)	57 (70)
150	-0.256 (-0.200)	-0.393 (-0.265)	50 (63)
75	-0.264 (-0.192)	-0.322 (-0.208)	40 (51)

rates of all processes that involve peroxide loss, i.e., the reduction, the decomposition, and the peroxide transport to the anode compartment<sup>8</sup>.

The potentials of the electrodes studied are more positive<sup>\*</sup> at an outlet pressure of 0.2 MPa than at atmospheric pressure (see Tables I and II). This is due to increased solubility of oxygen, and hence increased rate of its reduction (see Eq. (14) in our previous paper<sup>8</sup>). Accordingly, there is also an increase in the yield of peroxide at this pressure, since the greatest loss of peroxide in trickle-bed electrodes of this type, that due to its reduction, decreases with positive shift in the potential.

In some measurements we observed a negative shift in the electrode potential with further increase in the pressure. This phenomenon can be explained in the same way as the effect of increased electrolyte flow rate, i.e., by a reduction in the gas-liquid interfacial area and the consequent drop in the rate of oxygen transport.

That the proportion of gas within the interparticle pores of the electrode decreases considerably with increase in pressure has been confirmed by measurements of the liquid hold-up. For a trickle-bed electrode of 0.18–0.4 mm graphite particles, an electrolyte flow rate of 0.15 dm<sup>3</sup> h<sup>-1</sup>, and a gas flow rate of 0.56 dm<sup>3</sup> min<sup>-1</sup>, for example, the overall proportion of electrolyte increased from 74 to 96% on increasing the overpressure at the outlet from 0 to 0.5 MPa.

We observed rather large differences (by up to 0.2 V) between the potentials  $E'$  measured at the same distance from the current collector, but at various places of the electrode. However, even an evaluation of a large number of data did not reveal any correlation between the potential and the distance from the place of the mixture inflow.

We assume that the considerable spread in the values of local potential is caused by two phenomena. One is irregular compression of the electrode material, resulting in large local differences in both the resistance of crushed graphite and the voltage loss,  $\Delta(\phi t)$ . The other is irregular distribution of the gas and liquid phases, and the consequent differences in the local values of the mass transfer coefficients, and hence the overvoltage.

This explanation has been confirmed by measurements in which the large nickel mesh was replaced by 5 × 20 mm strips inserted between the crushed graphite and the diaphragm opposite to the mouths of the potential probes. The local values of  $\Delta\phi(t)$  showed a considerable scatter: the standard deviations were 10 to 60% of the measured voltages. A further indication of the nonuniformity of current densities is found in large differences between the potentials  $E(t)$  measured by the individual probes. The relative standard deviations of the overvoltages range between 0.1 and 0.4.

The characteristic quantities used to compare various trickle-bed electrodes were the potentials  $E'(t)$  and  $E(t)$  at the diaphragm. Polarization curves for trickle-bed electrodes prepared from various crushed graphite fractions are shown in Fig. 5. It is seen that the potentials shift to much more positive values with decreasing

grain size. This is due to increasing surface area of electrodes, and also to an increased pressure loss<sup>9</sup> and the consequent increase in the mass transfer coefficients<sup>8</sup>.

The more rapid potential drop in electrodes with coarser graphite fractions results in a marked enhancement of the rate of peroxide reduction with increasing current density and a sharper fall in the current yields of hydrogen peroxide<sup>9</sup>.

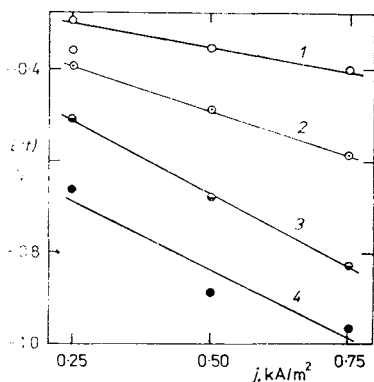


FIG. 5

Variation in the potential,  $E(t)$ , with the current density for crushed graphite electrodes with various sieve fractions; 1 0.08 to 0.18 mm; 2 0.18–0.4 mm; 3 0.4–0.63 mm; 4 0.63–1 mm. Volpor diaphragm; electrolyte flow rate,  $0.15 \text{ dm}^3 \text{ h}^{-1}$ ; oxygen flow rate,  $86 \text{ dm}^3 \text{ h}^{-1}$

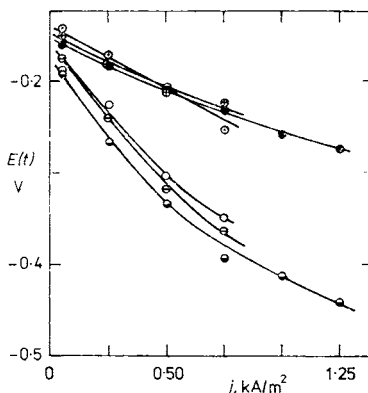


FIG. 6

Variation in the potential,  $E(t)$ , with the current density for a crushed graphite (fraction II) electrode separated by a Nafion 295 ionex membrane. Key as in Fig. 3

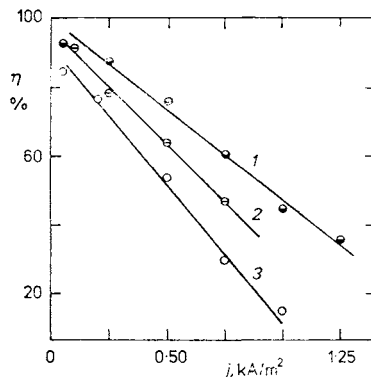


FIG. 7

Variation in the current yield of hydrogen peroxide with the current density. Experimental conditions are the same as those of Fig. 6



From the viewpoint of the potential, the optimum trickle-bed electrode for making hydrogen peroxide by oxygen reduction is that with the finest graphite particles. A drawback of this electrode is, however, an increase in the peroxide loss by decomposition<sup>8</sup>.

The highest current yields of hydrogen peroxide were achieved with electrodes of fraction II (see our previous paper<sup>9</sup>). Here, the decrease in the potential with increasing current density was relatively small, and the rate of peroxide decomposition was slower than that for the finest fraction.

The use of an ionex membrane in the cell eliminates the parallel flows of gas and electrolyte through the anode compartment, which were observed when the electrodes were separated by a diaphragm<sup>9</sup>. With an ionex membrane, the linear velocities of gas and liquid are higher at the same flow rates, and the same is true for the pressure loss. This is why the mass transfer coefficients are higher in this set-up and the electrode potentials attain more positive values. This has been confirmed by measurements of various trickle-bed electrodes. For example, comparison of the curves in Fig. 6 with curve 2 in Fig. 5 indicates that, at an electrolyte flow rate of  $0.15 \text{ dm}^3 \cdot \text{h}^{-1}$ , the electrode potentials in the ionex membrane are by 0.2 to 0.3 V more positive than those observed in the diaphragm set-up. There is, however, an additional effect which contributes to increased current yields of hydrogen peroxide in the electrolysis with a membrane, and that is hindrance to the transport of perhydroxyl ions towards the anode. This arrangement therefore provides relatively good peroxide yields at the outlet from the trickle-bed electrode even at atmospheric pressure (see Fig. 7), by 20 to 40% exceeding those obtained under the same conditions by electrolysis with a diaphragm. The maximum peroxide concentration at the outlet of the cathode was  $0.55 \text{ mol dm}^{-3}$  at atmospheric pressure, and  $0.75 \text{ mol dm}^{-3}$  at a pressure of 0.5 MPa.

The above described measurements have indicated that the optimum performance of trickle-bed electrodes for oxygen reduction to hydrogen peroxide requires such conditions that are conducive to as positive values of the electrode potentials as possible. Among the conditions are the use of fine graphite fractions and an ionex membrane, high oxygen flow rate, high pressure, and sufficient compression of the electrode material (0.1 MPa at the minimum).

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